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(19) (CA) **CANADIAN PATENT** (12)

(54) 2-CYANO-2-HYDROXYIMINOACETAMIDES AND
ACETATES AS PLANT DISEASE CONTROL AGENTS

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ABSTRACT OF THE DISCLOSURE

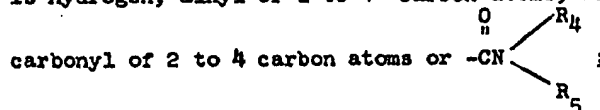
Compounds of the formula



wherein R is hydrogen; alkyl of 1 to 13 carbon atoms; alkyl of 1 to 13 carbon atoms substituted with alkoxy carbonyl of 2 to 4 carbon atoms; acyl of 2 to 4 carbon atoms; acyloxy of 2 to 4 carbon atoms or cyano; acyl of 1 to 4 carbon atoms; alkoxy carbonyl of 2 to 4 carbon atoms; aralkyl of 7 to 10 carbon atoms; or a metal selected from the group consisting of sodium, potassium, calcium, manganese, zinc, copper and iron;

R₁ is alkoxy of 1 to 4 carbon atoms or -NR₂R₃;

R₂ is hydrogen, alkyl of 1 to 4 carbon atoms; alkoxy-

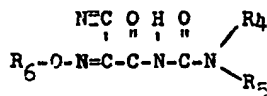


R₃ is hydrogen or alkyl of 1 to 4 carbon atoms, with the proviso that R₃ is H when R₂ is alkoxy carbonyl or -C(=O)NR₄R₅;

R₄ and R₅ may be the same or different and are hydrogen or alkyl of 1 to 4 carbon atoms; and

X is oxygen or sulfur;

are useful in preventing fungus diseases of plants. Of the compounds described above, the compounds



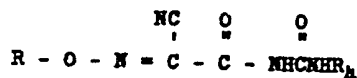
where R₄ and R₅ are defined as above and R₆ is alkyl of 1 to 13 carbon atoms; alkyl of 1 to 13 carbon atoms substituted

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with alkoxy carbonyl of 2 to 4 carbon atoms, acyl of 2 to 4 carbon atoms, acyloxy of 2 to 4 carbon atoms or cyano; acyl of 1 to 4 carbon atoms; or aralkyl of 7 to 10 carbon atoms are novel. Of the novel compounds, the compound wherein R_4 and R_5 are hydrogen and R_6 is methyl is preferred. In the Supplementary Disclosure 2-cyano-2-methoxyimino-N-methylcarbamoylacetamide, 2-cyano-N-ethylcarbamoyl-2-methoxyiminoacetamide, 2-cyano-2-ethoxyimino-N-ethylcarbamoylacetamide; 2-cyano-2-methoxyimino-N-propylcarbamoylacetamide and compounds of the formula



wherein

R_4 is hydrogen, alkyl of 1 to 4 carbon atoms or allyl, and

R is alkyl of 1 to 13 carbon atoms, cycloalkyl of 5 to 7 carbon atoms or alkenyl of 3 to 6 carbon atoms, provided that when R is alkyl, R_4 is allyl,

are also disclosed as being useful in preventing fungus diseases in plants.

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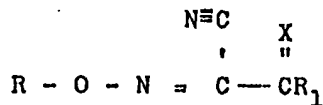
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BACKGROUND OF THE INVENTION

This invention relates to a class of compounds which are useful in controlling diseases of plants. Fungi and other disease incitants cause extensive losses in crops annually. While there are commercially available materials effective in preventing many plant diseases, still further improvement in this art is needed if full food and fiber production is to be realized. The compounds of this invention are particularly effective for the control of fungus plant diseases like potato late blight and downy mildews. In addition, the compounds of this invention exhibit systemic and curative properties. Relatively small amounts of material can be used to eradicate or cure existing plant disease caused by fungi. This is in contrast to most conventional protective materials which must be applied in advance of attack.

SUMMARY OF THE INVENTION

Compounds of the formula



20 Wherein R is hydrogen; alkyl of 1 to 13 carbon atoms;



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alkyl of 1 to 13 carbon atoms substituted with
alkoxycarbonyl of 2 to 4 carbon atoms, acyl
of 2 to 4 carbon atoms, acyloxy of 2 to 4
carbon atoms or cyano; acyl of 1 to 4 carbon
atoms; alkoxycarbonyl of 2 to 4 carbon atoms;
aralkyl of 7 to 10 carbon atoms; or a metal
selected from the group consisting of sodium,
potassium, calcium, manganese, copper and iron;

R_1 is alkoxy of 1 to 4 carbon atoms or $-NR_2R_3$;

10 R_2 is hydrogen, alkyl of 1 to 4 carbon atoms; alkoxy-

carbonyl of 2 to 4 carbon atoms or $-C(=O)NR_4R_5$;

R_3 is hydrogen or alkyl of 1 to 4 carbon atoms, with the
proviso that R_3 is H when R_2 is alkoxycarbonyl or
 $-C(=O)NR_4R_5$;

O

R_4 and R_5 may be the same or different and are hydrogen or
alkyl of 1 to 4 carbon atoms; and

X is oxygen or sulfur;

are useful in controlling fungus diseases of plants. Applica-
tion of these compounds to the locus to be protected from
20 disease effectively prevents the debility. These compounds
are also systemic and curative in plants. Because they are
curative, the compounds can be applied before or after the
plants to be protected are infected by fungi. This curative
activity makes the compounds useful in this invention

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particularly valuable for combination and application with conventional fungicides. Because the compounds are systemic in plants, the compounds can be applied not only directly to the infected plant parts, but also to uninfected parts of the plant, the seeds or to the soil. All of these application sites are included within the term "locus to be protected".

Of the compounds described above, those preferred for use in this invention are those where X is oxygen, R is hydrogen, alkyl of 1 to 13 carbon atoms, acyl of 1 to 4 carbon atoms, 10 alkoxy carbonyl of 2 to 4 carbon atoms, sodium, potassium, calcium, manganese, zinc, copper or iron and R_1 is $-NH_2$, $-NHCH_3$ or $-NH-\underset{\text{O}}{\underset{|}{C}}-NH_2$. More preferred are the compounds where R is hydrogen, alkyl of 1 to 13 carbon atoms or acetyl and R_1 is $-NH_2$, $-NHCH_3$ or $-NH-\underset{\text{O}}{\underset{|}{C}}-NH_2$. The most preferred compounds are 2-cyano-2-hydroxyiminoacetamide, 2-cyano-2-methoxyiminoacetamide, N-carbamoyl-2-cyano-2-methoxyiminoacetamide and 2-acetoxyimino-2-cyano-N-methyl acetamide.

Effective compositions of the compounds described above consist essentially of one of the above compounds and 20 an inert diluent. Surfactants can also be included as well as other ingredients which do not detract from the effectiveness of the active compound.

DETAILED DESCRIPTION OF THE INVENTION

The compounds useful in this invention are in part known and can be made as described in the literature or by known methods.

2-Cyano-2-hydroxyiminoacetamide ($H_2N-\underset{\text{O}}{\underset{|}{C}}-\underset{\text{O}}{\underset{|}{C}}-CN$) can be

made by nitrosation of cyanoacetamide with sodium nitrite and

1040530

acetic acid as described by M. Conrad and A. Schulze, Ber. 42, 738 (1909). These authors also describe the preparation of 2-cyano-2-hydroxyimino-N-ethoxycarbonylacetamide

$$(C_2H_5OOC-\overset{H}{\underset{O}{\underset{N-OH}{\parallel}}}{C}-C-CN)$$

from cyanoacetylurethane by the same method [Ber. 42, 742 (1909)].

2-Cyano-2-hydroxyimino-N-carbamoylacetamide

$$(H_2N-\overset{H}{\underset{O}{\underset{N-OH}{\parallel}}}{C}-C-CN)$$

is prepared as described by Conrad and Schulze (see above, p. 740, 741) from cyanoacetylurea and sodium nitrite followed by acidification.

10 Salts of these oximes can be made by slurring the free oxime in water, adding an aqueous solution of an equivalent amount of the appropriate base, such as sodium or potassium hydroxide, warming the mixture until the solid is dissolved, and vacuum concentrating the solution.

2-Cyano-2-methoxyiminoacetamide ($H_2N-\overset{H}{\underset{O}{\underset{N-OCH_3}{\parallel}}}{C}-C-CN$) can

be prepared by methylation of 2-cyano-2-hydroxyiminoacetamide (see above) with dimethyl sulfate and aqueous potassium hydroxide as described by O. Diels and E. Borgwardt, Ber. 54, 1342 (1921). The higher alkoxyimino homologs can be conveniently prepared by alkylating the sodium salt of 2-cyano-2-hydroxyiminoacetamide with the appropriate alkyl halide in DMF. For example, 2-cyano-2-n-dodecyloxyiminoacetamide

20 ($H_2N-\overset{H}{\underset{O}{\underset{N-O-C_{12}H_{25}}{\parallel}}}{C}-C-CN$) mp 84-6°, can be prepared by dissolving

the sodium salt of 2-cyano-2-hydroxyiminoacetamide in dimethylformamide. While stirring, 1-iodododecane is added and the

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solution is heated on the steam bath for six hours. After cooling to room temperature, the solution is poured into water and the precipitate is collected on a filter, washed with water and dried.

The corresponding n-octyl derivative, 2-cyano-2-n-octyloxyiminoacetamide, mp 84-6°, is made from the above sodium salt and 1-bromooctane in the same way. Similarly, the corresponding n-decyloxy derivative, 2-cyano-2-n-decyloxyiminoacetamide, mp 86-7°, made from the above sodium salt and 1-iododecane. The tridecyl derivative also melts at 86-7°.

Substituted alkyl derivatives or alkenyl derivatives are made in the same way. The following table lists a number of such materials by way of example: $\text{H}_2\text{N}-\underset{\text{O}}{\underset{\text{N-O-R}}{\text{C}}}-\text{C}-\text{CN}$

<u>R =</u>	<u>mp</u>
$-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_5$	88-9°
$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CN}$	77-80°
$-\text{CH}_2-\text{COOC}_2\text{H}_5$	143.5-44°
$-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CH}_3$	120-1°
$-\text{CH}_2-\text{CH}_2-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CH}_3$	90-1°
$-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}-\text{C}_6\text{H}_5$	146-7°
$-\text{CH}_2-\text{CH}=\text{CH}_2$	78-9°

N-carbamoyl-2-cyano-2-methoxyiminoacetamide, mp 161-3°, is similarly prepared from the sodium salt of 2-cyano-2-hydroxyimino-N-carbamoylacetamide and methyl iodide in DMF.

1040530

Additional novel compounds of this invention that are prepared by conventional alkylation, aralkylation, acylation, alkoxycarbonylation and carbamoylation reactions are:

N-carbamoyl-2-cyano-2-n-octyloxyiminoacetamide, m.p. 75-7°

N-carbamoyl-2-cyano-2-n-dodecyloxyiminoacetamide, m.p. 81-4°

N-carbamoyl-2-cyano-2-(3-phenylpropyl)oxyiminoacetamide,
m.p. 108-9°

N-carbamoyl-2-cyano-2-acetoxyminoacetamide, m.p. 182-3°

10 N-dimethylcarbamoyl-2-cyano-2-methoxyiminoacetamide.

2-Cyano-2-methoxyiminoacetic acid, ethyl ester
($\text{C}_2\text{H}_5\text{-OOC}-\underset{\text{N-OCH}_3}{\overset{\text{O}}{\text{C}}}\text{-CN}$) is prepared from the corresponding oxime

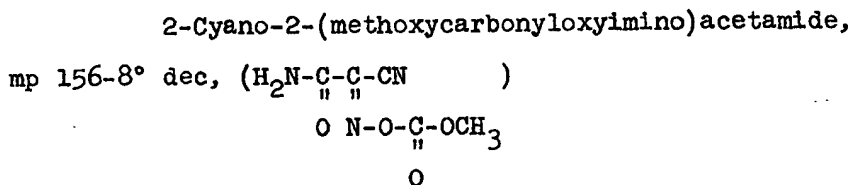
salt by methylation as described by Muller (Bull. Soc. Chim. [37, 27, 105]). The higher homologs of this material can be prepared in the same way from the higher esters of cyanoacetic acid. For example, the sec-butyl esters are prepared from sec-butyl cyanoacetate via oximation and reaction of the sodium salt of the oxime with the appropriate halide, for example n-decyl iodide.

20 2-Cyano-2-acetoxyminoacetamide ($\text{H}_2\text{N}-\underset{\text{O N-O-C-CH}_3}{\overset{\text{O}}{\text{C}}}\text{-CN}$),
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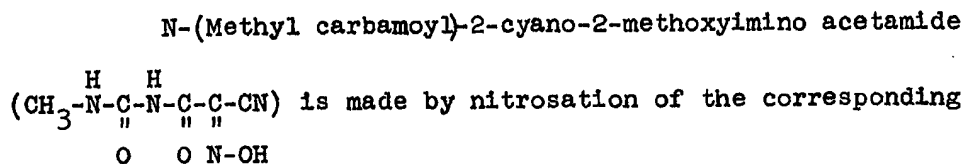
described by Diels and Borgwardt (see above) is conveniently prepared by introducing ketene gas into a solution of 2-cyano-2-hydroxyiminoacetamide in a suitable solvent such as acetonitrile followed by evaporation of the solvent. The higher acyl analogs can be prepared by reaction of the oxime with

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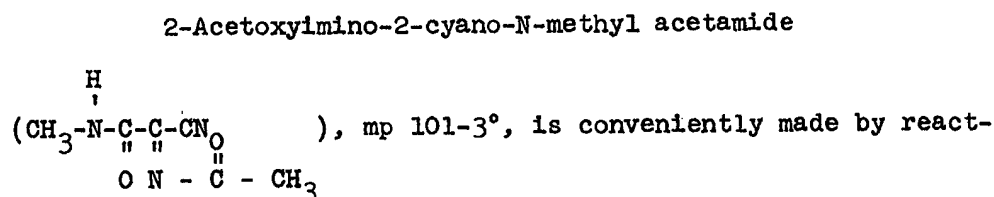
the appropriate anhydride, for example propionic anhydride, or with the appropriate acyl chloride, for example n-butyryl chloride, in the presence of a suitable base such as pyridine or triethylamine.



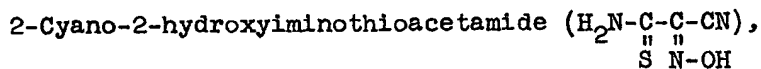
is prepared by adding dropwise methyl chloroformate to an aqueous slurry of the sodium salt of 2-cyano-2-hydroxyimino-acetonitrile with stirring and cooling. The higher alkoxy-carbonyl homologs, for example 2-cyano-2-(butoxycarbonyloxy-
 10 imino)acetamide, are made in the same way from the corresponding higher alkyl chloroformates, e.g., butyl chloroformate.



N-(methyl carbamoyl)-2-cyanoacetamide in acetic acid as described in German Patent DRP 227,390 (Frdl 10, 177)



ing the corresponding free oxime with ketene in acetonitrile.
 20 This free oxime (mp 210-1°) is made by nitrosation of N-methyl acetamide.



1040530

mp 145° dec, can be prepared from 2-cyanothioacetamide, sodium nitrite and hydrochloric acid as described by G. Shaw and D. N. Butler, J. Chem. Soc. 1959, 4042. The corresponding methyl ester, 2-cyano-2-methoxyiminothioacetamide
($\text{H}_2\text{N}-\underset{\text{S N-OCH}_3}{\overset{\text{CN}}{\text{C}}}-\underset{\text{CN}}{\text{C}}$) mp 163-5°, can be prepared either by methyl-

ation of the oxime with dimethylsulfate in aqueous KOH or by reacting 2-cyano-2-methoxyiminoacetamide in a known manner with P_2S_5 .

10 The compounds useful in this invention are active plant disease control agents. They have qualities of systemic and curative activity when applied to soil, to seed or propagation pieces, or to foliage. Combinations with other plant protectants especially fungicides, provide exceptional disease control. The systemic and curative properties of the disease control agents of this invention make their combination with fungicides usually result in more than an additive effect. For this reason, compositions containing a combination of a fungicide and a compound of this case are preferred. The unique systemic property of the compounds of this case is
20 strikingly evident by the control of the potato late blight disease on the untreated foliage when treatments with the compounds of this invention are applied solely to the root system. Additional evidence comes from the protection of untreated new growth on plants which had previously been sprayed with the compounds of this invention. Still further evidence comes from the curative action against established infections by the causal agent of late blight disease. The disease can be arrested even when treatments are delayed hours

after plants have been artificially inoculated.

Of the fungi causing diseases on agricultural crops, those classed as Phycomycetes are among the most virulent. The disorders caused by this group of fungi include late blight of tomatoes and potatoes, downy mildew of grapes and cucurbits, and Pythium root rots. Diseases caused by Phycomycetes are especially susceptible to control by the compounds of this invention. Many other plant diseases of primary importance to the agriculturist are also controlled.

10

The many diseases (along with their causal agents) against which the compounds and methods of this invention are effective may be represented by, but are not limited to, the following: Phytophthora infestans, which causes late blight of potato and tomato; Phytophthora cinnamomi, which causes root rot of many perennial plants and heart rot of pineapple; Alternaria solani, which attack plants in the Cruciferae, Cucurbitaceae, Umbelliferae, and Solanaceae families; and Venturia inaequalis, which causes apple scab.

20

The compounds of this invention provide protection from damage caused by certain fungi when applied to the proper locus by the methods described hereinafter and at a sufficient rate to exert the desired effect. They are especially suited for the protection of living plants by applying the compounds of this invention to the soil in which they are growing or in which they may subsequently be seeded or planted, to seeds, tubers, bulbs, or other plant reproductive parts prior to planting, as well as to foliage, stems, and/or fruit. Soil applications are made from dusts, granules, pellets, solutions, or slurries.

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Preferred rates for application of the compounds

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of this invention to soil in which plants are or will be growing range from 1 to 500 parts per million by weight of the soil in which the roots are or will be growing. More preferred use rates are in the range of 5 to 200 parts per million. The most preferred rates are in the range of 10 to 100 parts per million. Preferred rates for application to seeds, tubers, bulbs, or other plant reproductive parts range from 0.5 to 100 grams of active compound of this invention per kilo of planting material treated. More preferred rates are in the range of 1 to 75 grams of active compound per kilo. The most preferred rates are in the range of 2 to 50 grams per kilo. Applications of this type are made from dusts, slurries, or solutions.

Preferred rates of application for the compounds of this invention to foliage, stems, and/or fruit of living plants range from 0.1 to 20 kilograms of active ingredient per hectare. More preferred rates are in the range of 0.2 to 10 kilos per hectare. The most preferred rates are in the range of 0.5 to 5 kilograms per hectare. The optimum amount within this range depends upon a number of variables which are well known to those skilled in the art of plant protection. The variables include, but are not limited to, the disease to be controlled, weather conditions expected, the type of crop, stage of development of the crop, and the interval between applications. Applications within the range given may need to be repeated one or many more times at intervals of 1 to 60 days. Applications are made from dusts, slurries, or solutions.

The compositions of the invention can contain, in addition to the active ingredient of this invention, conven-

1040530

tional insecticides, miticides, bactericides, nematocides, fungicides, or other agricultural chemicals such as fruit set agents, fruit thinning compounds, fertilizer ingredients and the like. The additional agricultural chemicals are employed in mixtures or combinations in amounts ranging from one-tenth to twenty times that of the compound or compounds of this invention. The proper choice of amounts is readily made by one skilled in the art of protecting plants from pest depredations. The following are illustrative of the agricultural chemicals that may be included in compositions of the compounds of this invention or, additionally, that may be added to sprays containing one or more of the active compounds of this invention:

bis(dimethylthiocarbamoyl)disulfide; or tetramethylthiuram disulfide (thiram);

metal salts of ethylenebisdithiocarbamic acid or propylenebisdithiocarbamic acids, e.g. manganese, zinc, iron and sodium salts (maneb or zineb);

n-dodecylguanidine acetate (dodine);

N-(trichloromethylthio)phthalimide (folpet);

N-[(trichloromethyl)thio]-4-cyclohexene-1,2-dicarboximide (captan);

cis-N-[(1,1,2,2-tetrachloroethyl)thio]-4-cyclohexene-1,2-dicarboximide (captofol);

2,4-dichloro-6-(o-chloroanilino)-s-triazine ("Dyrene");

3,3'-ethylenebis(tetrahydro-4,6-dimethyl-2H-1,3,5-thiadiazine-2-thione), (milneb);

triphenyltin hydroxide (fentin hydroxide);

triphenyltin acetate (fentin acetate);

N'-dichlorofluoromethylthio-N,N-dimethyl-N'-

1040530

phenylsulfamide (dichlofluanid);

tetrachloroisophthalonitrile (chlorothalonil);

tribasic copper sulfate;

fixed copper;

sulfur;

methyl-1-(butylcarbamoyl)-2-benzimidazolecarbamate
(benomyl);

methyl-2-benzimidazolecarbamate;

1,2-bis(3-methoxycarbonyl-2-thioureido)benzene

10 (methyl thiophanate);

The agricultural chemicals listed above are merely exemplary of the compounds which can be mixed with the active compounds of this invention and are not intended to any way limit the invention.

The use of pesticides in combination with a compound within the scope of this invention sometimes appears to greatly enhance the activity of the active compound of the invention. An unexpected degree of activity is sometimes seen when another pesticide is used along with the methods
20 of this invention.

The useful compounds can be applied in a variety of formulations, including wettable powders, water-soluble powders, suspensions, emulsifiable concentrates, dusts, solutions, granules, pellets, etc. High strength compositions may also be prepared for use by local formulators in further processing.

These formulations include one or more compounds useful in this invention, and can include surface-active agents, solid or liquid diluents and other materials as required to
30 produce the desired formulation.

1040530

The surface-active agents act as wetting, dispersing and emulsifying agents which assist dispersion of the active material in a spray, and improve wetting of waxy foliage and the like by the spray. Thus they aid in convenience, accuracy and effectiveness in use. The surfactants can include such anionic, non-ionic and cationic agents as have been used heretofore in pesticidal compositions of similar type. A detailed list of such agents may be found in "Detergents and Emulsifiers Annual", (John W. McCutcheon, Inc.). Addition of surfactants also prevents precipitation of large crystals of the active compounds on plant surfaces and improves penetration of the active compounds, thus increasing activity. Anionic and non-ionic surfactants are preferred. Such preferred surfactants include alkali and alkaline earth salts of alkylarylsulfonic acids, such as dodecylbenzenesulfonates and alkyl-naphthalene-sulfonates, dialkyl sodium sulfosuccinate esters, sodium lauryl sulfate, sodium N-methyl-N-oleoyltaurate, sodium dodecyldiphenyl ether disulfonate and the oleic acid ester of sodium isethionate. Other preferred surfactants include alkyl and alkylphenyl polyethylene glycol ethers, and their phosphate derivatives, polyoxyethylene derivatives of sorbitan fatty esters and long-chain alcohols and mercaptans, as well as polyoxyethylene esters of fatty acids. Film forming water-soluble polymers may be used in place of surfactants to improve activity. Humectants and oils chosen for low phytotoxicity also contribute to enhanced activity of the compositions of this invention. White oils having a viscosity of about 150 S.S.U. or higher are preferred.

Further information on formulation of the active compounds described above into the fungicidal compositions

1040530

of this invention can be found in J. B. Buchanan, U.S. 3,576,834 (4/27/71), R. R. Schaffen, U.S. 3,560,616 (2/2/71) and E. Somers, "Formulation", Chapter 6 in Torgeson, "Fungicides", Vol. I, Academic Press, New York, 1967.

The following examples further illustrate the invention. All parts and percentages are by weight.

EXAMPLE 1

A wettable powder formulation can be made and applied as follows:

	<u>Percent</u>
2-cyano-2-hydroxyiminoacetamide	50
sodium alkylnaphthalenesulfonate	2
low-viscosity methylcellulose	2
diatomaceous earth	46

The ingredients are blended, coarsely hammer-milled and then air-milled to produce particles of active essentially all below 20 microns in diameter. The product is reblended before packaging.

All compounds of the invention may be formulated similarly.

This formulation is dispersed in water in an amount sufficient to provide a concentration of 400 ppm of the active compound of this invention. A portion of this is diluted to a concentration of 80 ppm. The dispersions are sprayed to the point of run-off on potted tomato plants and allowed to dry. Both treated and untreated plants are inoculated with a spore suspension of Phytophthora infestans and incubated for a day in a saturated humidity chamber. After five days of additional incubation in the greenhouse, all of the untreated tomatoes are dead because of late blight

1040530

disease. The plants treated with the 80 ppm concentration have only an occasional confined lesion, whereas those treated with the 400 ppm concentration are completely healthy with no sign of disease. The other compounds of this invention can be substituted for 2-cyano-2-hydroxyiminoacetamide with like results. For example, N-carbamoyl-2-cyano-2-methoxyiminoacetamide and 2-acetoxyimino-2-cyano-N-methyl acetamide are particularly effective.

EXAMPLE 2

10 The formulation of Example 1 can be mixed in a spray tank with the fungicide, benomyl. This formulation is diluted to a concentration of 500 ppm of the active ingredient. The benomyl in the mixture is at a concentration of 100 ppm. Sprays are applied to the point of run-off each week during the growing season to a cucumber field subject to infection by the downy mildew fungus, Pseudoperonospora cubensis, the powdery mildew fungus, Erysiphe chichoracearum, and the gummy stem blight fungus, Mycosphaerella citrullina. The plants which are sprayed with this mixture are healthy
20 and bear a normal crop.

EXAMPLE 3

Potted greenhouse grown tomato plants are inoculated by spraying them with a spore suspension of P. infestans. They are incubated in a saturated humidity chamber for eight hours. The infected tomato plants are removed from the incubation chamber long enough to spray them with various disease control agents and combinations of these agents. The formulation of Example 1 is dispersed at a concentration of 400 ppm of the active ingredient. Similar dispersions are
30 made of the commercial fungicides, maneb, captafol, metiram,

1040530

and chlorothalonil. Additional treatments are made by mixing each of these dispersions of commercial fungicides with an equal quantity of the formulation of this example. This results in 200 ppm of each of the two component active ingredients. Six infected plants are sprayed with enough dispersion to have run-off of dry plants. After treatment, the plants are returned to the humidity chamber for a total of 24 hours. After an additional five days incubation in the greenhouse, the untreated plants are dead because of the late blight disease. Those plants treated with the commercial fungicides are completely defoliated. The plants treated with the formulation of this invention have only a few restricted lesions. Most of the foliage is healthy. This is because of the unique curative action of the compounds of this invention. The best control is afforded by the mixtures of commercial fungicides and the 2-cyano-2-hydroxyiminoacetamide.

EXAMPLE 4

Healthy uninoculated tomato plants are spray treated with the suspensions and mixtures prepared for the curative test described in Example 3. The treated plants are grown for five days in the greenhouse before they are inoculated with a spore suspension of P. infestans. The plants had grown sufficiently from the time they were treated to expose untreated foliage. After incubation, the untreated plants are dead because of late blight infections. The commercial fungicides provide good control on most of the foliage, but the newly expanded foliage is unprotected and is heavily blighted. The plants sprayed with the formulation of this invention have only a few blight lesions. The most striking feature is the reduction in infections on the newly

1040530

expanded foliage. This is because of the systemic property of protecting untreated plant parts afforded by the compounds of this invention. Those plants which are treated with mixtures of 2-cyano-2-hydroxyiminoacetamide and commercial fungicides at one-half rate of each are the healthiest of all.

EXAMPLE 5

A wettable powder formulation can be prepared as follows:

	<u>Percent</u>
10 N-carbamoyl-2-cyano-2-methoxyimino- acetamide	80
sodium alkylnaphthalenesulfonate	2
sodium ligninsulfonate	2
synthetic amorphous silica	3
Kaolinite	13

The ingredients are thoroughly blended, passed through a hammer-mill to produce an average particle size under 40 microns, reblended and sifted through a U.S.S.No. 50 sieve (0.3 mm openings) before packaging.

20 This formulation can be applied as follows: A potato field is selected in which there is a uniform but light infection of the late blight disease. The older foliage of each plant supports one or two sporulating Phytophthora infestans lesions. The plant damage at this point is slight, but the potential for disease spread is high. Plots are designated as five rows wide and 20 meters long. Treatments are assigned to various plots randomly through the field leaving much of the field untreated as buffers between treated plots. A series of treatments is selected
30 for application immediately following weather conditions

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conducive to disease spread. Among those treatments is the formulation of this Example dispersed in water at a concentration of 1,000 ppm of active ingredient. Other treatments are a representation of commercially available fungicides such as maneb, captofol, and chlorothalonil, applied at their recommended use rate. In addition to these single compound applications, combinations of the formulation of this Example with each of the commercial fungicides are made at rates of 1/2 of that used alone. Spray applications are made immediately after an overnight rain which had the potential of spreading the disease. After a week, the untreated foliage in this field is completely killed by the late blight disease. Those plots receiving treatments of commercial fungicides are severely diseased and are more than 80% defoliated. Those plots receiving the formulation of this Example are protected from the late blight disease. Those plots receiving treatments of commercial fungicides are severely diseased and are more than 80% defoliated. Those plots receiving the formulation of this Example are protected from the late blight disease and are only slightly defoliated. Those plots receiving the combination of the formulation of this invention plus a commercial fungicide are healthy and green and free of disease. Other commercial fungicides such as metiram, "Daconil 2787" and zineb, can also be used with like results. The other compounds of this invention may be substituted for 2-cyano-2-hydroxyiminoacetamide with like results.

EXAMPLE 6

An aqueous suspension can be prepared and applied as follows:

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	<u>Percent</u>
2-cyano-2-dodecyloxyiminoacetamide	25
hydrated attapulgite	3
crude calcium ligninsulfonate	10
disodium hydrogen phosphate	0.5
water	61.5

The ingredients are ground together in a ball or roller mill until the solid particles have been reduced to diameters under 10 microns.

- 10 This suspension is dispersed in water in an amount sufficient to provide a concentration of 400 ppm of the active compound of this invention. A portion of this is diluted to a concentration of 80 ppm. The dispersions are sprayed to the point of run-off on potted apple plants and allowed to dry. Both treated and untreated plants are inoculated with a spore suspension of Venturia inaequalis and incubated for a day in a saturated humidity chamber. After ten days of additional incubation in the greenhouse, all of the untreated apples have young susceptible leaves completely covered with
- 20 sporulating apple scab lesions. The plants treated with the 80 ppm concentration have only an occasional confined lesion, whereas those treated with the 400 ppm concentration are completely healthy with no sign of disease.

EXAMPLE 7

An oil suspension can be prepared as follows:

	<u>Percent</u>
2-cyano-2-hydroxyiminoacetamide	25
polyoxyethylene sorbitol hexaoleate	5
highly aliphatic hydrocarbon oil	70

- 30 The ingredients are ground together in a sand mill

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until the solid particles have been reduced to under about 5 microns. The resulting rather thick suspension may be applied directly, extended with oils, or emulsified in water.

This formulation can be applied in the same manner as the wettable powder formulation of Example 5 with similar results.

EXAMPLE 8

An emulsifiable concentrate can be prepared and applied as follows:

	<u>Percent</u>
10 2-cyano-2-dodecyloxyiminoacetamide	30
isophorone	65
blend of oil-soluble sulfonates and polyoxyethylene ethers	5

The ingredients are combined and stirred with gentle warming to speed solution. A fine screen filter is included in the packaging line to insure the absence of any undissolved matter in the final product.

20 The above formulation is dispersed in water to give an active ingredient concentration of 800 ppm. Eight uniform grapevines of the same variety are sprayed to run-off at weekly intervals during the growing season with the above formulation. Untreated vines growing near are severely infected with the downy mildew fungus, Plasmopora viticola. The eight treated vines are healthy with a normal crop of disease free fruit.

EXAMPLE 9

High-strength powder.

	<u>Percent</u>
2-cyano-2-hydroxyimino acetamide	90.0
30 fine silica	9.5
diactyl sulfosuccinic acid, disodium salt	0.5

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This powder is prepared by blending and then grinding in a hammer-mill. The formulation, when dispersed in water, causes the active ingredient to go into solution. The spray can be used in a manner similar to Example 5.

SUPPLEMENTARY DISCLOSURE

It has now been found that according to the present invention

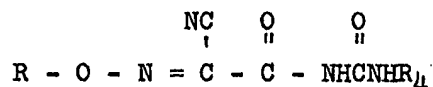
2-Cyano-2-methoxyimino-N-methylcarbamoylacetamide;

2-Cyano-N-ethylcarbamoyl-2-methoxyiminoacetamide;

10 2-Cyano-2-ethoxyimino-N-ethylcarbamoylacetamide;

2-Cyano-2-methoxyimino-N-propylcarbamoylacetamide

and compounds of the formula



wherein

R_4 is hydrogen, alkyl of 1 to 4 carbon atoms or allyl,
and

R is alkyl of 1 to 13 carbon atoms, cycloalkyl of 5 to 7 carbon atoms or alkenyl of 3 to 6 carbon atoms,
provided that when R is alkyl, R_4 is allyl

20 are useful in controlling fungus diseases of plants. Application of these compounds to the locus to be protected from disease effectively prevents the debility. These compounds are also systemic and curative in plants. Because they are curative, the compounds can be applied before or after the plants to be protected are infected by fungi. This curative activity makes the compounds useful in this invention particularly valuable for combination and application with conventional fungicides. Because the compounds are systemic in plants, the compounds can be applied not only directly to the

infected plant parts, but also to uninfected parts of the plant, the seeds or to the soil. All of these application sites are included within the term "locus to be protected". In addition to those compounds specifically named above, N-allylcarbamoyl-2-cyano-2-methoxyiminoacetamide is preferred.

Effective compositions of the compound described above consist essentially of one of the above compounds and an inert diluent. Surfactants can also be included as well as other ingredients which do not detract from the effectiveness of the active compound.

DETAILED DESCRIPTION OF THE INVENTION
OF THE SUPPLEMENTARY DISCLOSURE

2-Cyano-2-methoxyimino-N-methylcarbamoylacetamide

$$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ (\text{CH}_3-\text{N}-\text{C}-\text{N}-\text{C}-\text{C}-\text{CN}) \\ | \quad | \quad | \\ \text{O} \quad \text{O} \quad \text{N}-\text{OCH}_3 \end{array}$$
, M.P. 176-7°, was prepared by

methylation, with diazomethane in ether, the corresponding free oxime 2-cyano-2-hydroxyimino-N-methylcarbamoylacetamide, the preparation of which is described in German Patent No. 227,390 (Friedlander 10, 1177). This preparation involves the nitrosation of 1-cyanoacetyl-3-methylurea with sodium nitrile in aqueous acetic acid.

The next higher homolog, 2-cyano-N-ethylcarbamoyl-2-methoxyiminoacetamide, M.P. 160-1°, may be similarly prepared from 1-cyanoacetyl-3-ethylurea and sodium nitrile in aqueous acetic acid or other suitable acid such as hydrochloric acid followed by methylation of the oxime with diazomethane.

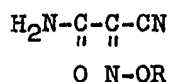
This methylation may also be carried out by dissolving the free oxime in dimethylformamide, adding a molar equivalent of a base such as sodium methoxide to convert the free oxime to a salt such as the sodium salt, adding methyl iodide (preferably in excess) and stirring the mixture at room temperature.

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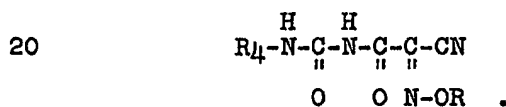
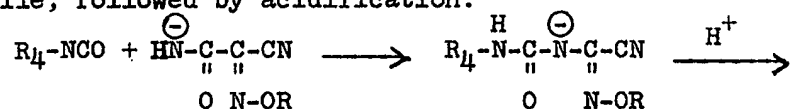
Methyl bromide may be used instead of methyl iodide. This method is quite suitable also for the preparation of the higher O-alkyl compounds, such as, for example, the propoxyimino derivative.

Another useful method for carrying out the methylation consists in refluxing the free oxime in acetone with powdered potassium carbonate and dimethyl sulfate. The use of a slight excess, for example, 10%, of the latter two reagents increases the yield of the methyl ether. The use of diethyl sulfate in this reaction affords the corresponding ethoxyimino compound.

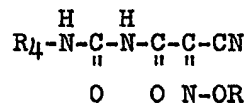
10 Yet another suitable method for preparing the ureas of this invention consists in reacting a compound of the general formula



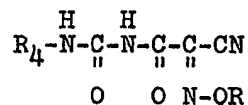
with a suitable base (for example, sodium hydride or sodium methoxide) in order to convert it to the anionic form, and in reacting this anion with an isocyanate of the general formula $\text{R}_4\text{-NCO}$ in a suitable inert solvent such as tetrahydrofuran or acetonitrile, followed by acidification:



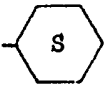

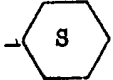
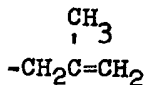
Other homologs of the general formula



can be made according to the methods described above. Their melting points are listed in the following table.



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<u>R₄ =</u>	<u>R =</u>	<u>M.P.</u>
C ₂ H ₅	C ₂ H ₅	121-2°
allyl	CH ₃	134-6°
n-C ₃ H ₇	CH ₃	121.5-3°
i-C ₃ H ₇	CH ₃	137.5-8.5°
H		178-180°
H	-CH ₂ CH=CH ₂	120-121°
C ₂ H ₅		110-112°
C ₂ H ₅		95-97°
10 C ₂ H ₅	-CH ₂ CHCH ₂	90-91.5°
C ₂ H ₅		92-93°

The compositions of the invention can contain, in addition to the active ingredient of this invention, conventional insecticides, miticides, bactericides, nematocides, fungicides, or other agricultural chemicals such as fruit set agents, fruit thinning compounds, fertilizer ingredients and the like. The additional agricultural chemicals are employed in mixtures or combinations in amounts ranging from one-tenth to twenty times that of the compound or compounds of this invention. The proper choice of amounts is readily made by one skilled in the art of protecting plants from pest depredations. The following are illustrative of the agricultural chemicals that may be included in compositions of

the compounds of this invention or, additionally, that may be added to sprays containing one or more of the active compounds of this invention:

bis(dimethylthiocarbamoyl)disulfide; or tetramethylthiuram disulfide (thiram);

metal salts of ethylenebisdithiocarbamic acid or propylenebisdithiocarbamic acids, e.g. manganese, zinc, iron and sodium salts (maneb or zineb) alone or admixed with zinc salts;

10 co-ordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb);

n-dodecylguanidine acetate (dodine);

N-(trichloromethylthio)phthalimide (folpet);

N-[(trichloromethyl)thio]-4-cyclohexene-1,2-dicarboximide (captan);

cis-N-[(1,1,2,2-tetrachloroethyl)thio]-4-cyclohexene-1,2-dicarboximide (captofol);

2,4-dichloro-6-(o-chloroanilino)- α -triazine ("Dyrene");

3,3'-ethylenebis(tetrahydro-4,6-dimethyl-2H-1,3,5-

20 thiadiazine-2-thione), (milneb);

triphenyltin hydroxide (fentin hydroxide);

triphenyltin acetate (fentin acetate);

N'-dichlorofluoromethylthio-N,N-dimethyl-N'-

phenylsulfamide (dichlorfluanid);

tetrachloroisophthalonitrile (chlorothalonil);

tribasic copper sulfate;

fixed copper;

sulfur;

methyl-1-(butylcarbamoyle)-2-benzimidazolecarbamate

(benomyl);

* denotes trade mark

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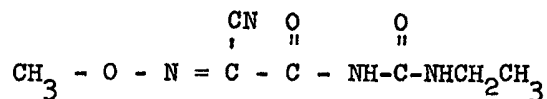
methyl-2-benzimidazolecarbamate;

1,2-bis(3-methoxycarbonyl-2-thioureido)benzene
(methyl thiophanate).

The agricultural chemicals listed above are merely exemplary of the compounds which can be mixed with the active compounds of this invention and are not intended to any way limit the invention.

The use of pesticides in combination with a compound within the scope of this invention sometimes appears to greatly enhance the activity of the active compound of the invention. An unexpected degree of activity is sometimes seen when another pesticide is used along with the methods of this invention.

A particularly preferred composition of the present invention is a compound of the formula



in combination with a fungicide selected from the following:

- A. manganese ethylenebisdithiocarbamate, admixed with inorganic zinc salts;
- 20 B. co-ordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb);
- C. zinc ethylenebisdithiocarbamate;
- D. fixed copper, such as basic copper sulfate, basic copper carbonate, copper oxychloride, and/or copper oxide;
- E. N-(trichloromethylthio)phthalimide (folpet);
- F. 2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil);
- G. cis-N-[(1,1,2,2-tetrachloroethyl)thio]-4-cyclohexene-1,2-dicarboximide (captafol);
- 30 H. triphenyltin hydroxide.

Broadly, the ratio of 2-cyano-N-(ethylcarbamoyl)-2-methoxyiminoacetamide to fungicides A-H in the combination is 10:1 to

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1:1000. Application of these combinations to the locus to be protected from disease effectively prevents the debility. Many of these combinations are also systemic and curative in plants. Because they are curative, the combinations can be applied before or after the plants to be protected are infected by fungi. Because the combinations are systemic in plants, they can be applied not only directly to the infected plant parts, but also to uninfected parts of the plant or to the soil. All of these application sites are included within the term "applying to the plants".

Effective compositions of the combinations described above consist essentially of one of the above combinations and an inert diluent. Surfactants can also be included as well as other ingredients which do not detract from the effectiveness of the combination.

Combinations of this invention which are especially preferred are 2-cyano-N-(ethylcarbamoyl)-2-methoxyiminoacetamide and one of the following compounds:

- A. manganese ethylenebisdithiocarbamate, admixed with inorganic zinc salts;
- B. co-ordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb);
- D. fixed copper, such as basic copper sulfate, basic copper carbonate, copper oxychloride, and/or copper oxide;
- E. N-(trichloromethylthio)phthalimide (folpet);
- H. triphenyltin hydroxide.

Additionally, a three-component combination of 2-cyano-N-(ethylcarbamoyl)-2-methoxyiminoacetamide, fungicide B and fungicide D may be utilized.

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Most preferred for exceptional disease control is the combination of 2-cyano-N-(ethylcarbamoyl)-1-methoxyiminoacetamide and the co-ordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb).

The combinations of this invention may contain the active ingredients, 2-cyano-N-(ethylcarbamoyl)-2-methoxyiminoacetamide and one of fungicides A-H, in the following ratios:

Broad: 10:1 to 1:1000

Preferred: 5:1 to 1:500

10 Most preferred: 2:1 to 1:100

The compounds and combinations of this invention are useful as plant disease control agents. Most have qualities of systemic and curative activity when applied to soil, to propagation pieces, to stems, or to foliage. The systemic and curative effects of the disease-control agents of this invention make a unique contribution to such combinations. The systemic property of the combinations of this case is strikingly evident in the control of potato and tomato late blight disease on the foliage when treatments with the combinations are applied solely to the root system. Additional evidence comes from the curative action against established infections by the causal agent of late blight disease. The disease can be arrested even when treatments are delayed hours after plants have been inoculated.

Of the fungi causing diseases on agricultural crops, those classed as Phycomycetes are among the most virulent. The disorders caused by this group of fungi include late blight of tomatoes and potatoes, as well as downy mildew of grapes, cole crops, legumes, and cucurbite. Diseases caused by Phycomycetes are susceptible to control by the compounds and especially by combinations of this invention.

The compounds and combinations of this invention provide protection from damage caused by certain fungi when applied to the proper locus by the methods described herein- after and at a sufficient rate to exert the desired effect. They are especially suited for the protection of living plants by applying the compounds or combinations of this invention to the soil in which they are growing or in which they may subsequently be seeded or planted, to seeds, tubers, bulbs, or other plant reproductive parts prior to planting, 10 as well as to foliage, stems, and/or fruit. Soil applications are made from dusts, granules, pellets, solutions, emulsions, or slurries.

Preferred rates for application of the compounds or the active ingredients of the claimed combinations to soil in which plants are or will be growing range from 0.5 to 500 ppm by weight of the soil in which the roots are or will be growing. More preferred use rates are in the range of 1 to 200 parts per million. The most preferred rates are in the range of 5 to 100 ppm. Preferred rates for application 20 to seeds, tubers, bulbs, or other plant reproductive parts range from 0.5 to 100 g. of active ingredients in the combinations of this invention per kilo of planting material treated. More preferred rates are in the range of 1-75 g. of active ingredients per kilo. The most preferred rates are in the range of 2-50 g. per kilo. Applications of this type are made from dusts, slurries, emulsions, or solutions.

Preferred rates of application for the compounds or combinations of this invention to foliage, stems, and/or fruit or living plants range from 0.1 to 30 kilograms of active 30 ingredients per hectare. More preferred rates are in the range of 0.2 to 20 kilos per hectare. The most preferred

rates are in the range of 0.3 to 10 kilograms per hectare. The optimum amount within this range depends upon a number of variables which are well known to those skilled in the art of plant protection. The variables include, but are not limited to, the disease to be controlled, weather conditions expected, the type of crop, stage of development of the crop, and the interval between applications. Applications within the range given may need to be repeated one or many more times at intervals of 1 to 60 days. Applications are made from
10 dusts, slurries, emulsions, or solutions.

The compounds and combinations can be applied in a variety of formulations, including wettable powders, water-soluble powders, suspensions, emulsifiable concentrates, dusts, solutions, granules, pellets, etc. High strength compositions may also be prepared for use by local formulators in further processing.

These formulations include the compounds or combinations of this invention, and can include surface-active agents, solid or liquid diluents and other materials as required to
20 produce the desired formulation.

The surface-active agents act as wetting, dispersing and emulsifying agents which assist dispersion of the active material in a spray, and improve wetting of waxy foliage and the like by the spray. Thus they aid in convenience, accuracy and effectiveness in use. The surfactants can include such anionic, non-ionic and cationic agents as have been used heretofore in pesticidal compositions of similar type. A detailed list of such agents may be found in "Detergents and Emulsifiers Annual", (John W. McCutcheon, Inc.). Addition
30 of surfactants also prevents precipitation of large crystals of the active compounds on plant surfaces and improves penetration of the active compounds, thus increasing activity.

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Anionic and nonionic surfactants are preferred. Such preferred surfactants include alkali and alkaline earth salts of alkylarylsulfonic acids, such as dodecylbenzenesulfonates and alkylnaphthalenesulfonates, dialkyl sodium sulfosuccinate esters, sodium lauryl sulfate, sodium N-methyl-N-oleoyltaurate, sodium dodecyldiphenyl ether disulfonate and the oleic acid ester of sodium isethionate. Other preferred surfactants include alkyl and alkylphenyl polyethylene glycol ethers, and their phosphate derivatives, polyoxyethylene derivatives of sorbitan fatty esters and long-chain alcohols and mercaptans, as well as polyoxyethylene esters of fatty acids. Film forming water-soluble polymers may be used in place of surfactants to improve activity. Humectants and oils chosen for low phytotoxicity also contribute to enhanced activity of the compositions of this invention. White oils having a viscosity of about 150 S.S.U. or higher are preferred.

Further information on formulation of the active compounds described above into the fungicidal compositions of this invention can be found in J. B. Buchanan, U.S. 3,576,834 (4/27/71), R. R. Schaffer, U.S. 3,560,616 (2/2/71) and E. Somers, "Formulation", Chapter 6 in Torgeson, "Fungicides", Vol. I, Academic Press, New York, 1967.

The following examples further illustrate the invention. All parts and percentages are by weight.

EXAMPLE 10

Potted greenhouse grown tomato plants are inoculated by spraying them with a spore suspension of P. infestans. They are incubated in a saturated humidity chamber at 20°C. for 20 hours. The infected tomato plants are removed from the incubation chamber long enough to spray them with various

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disease control agents. The compounds listed below are dispersed at a concentration of 80 ppm of the active ingredient. Three infected plants are sprayed with enough dispersion to have run-off dry plants. After treatment, the plants are placed in a greenhouse for an additional five days incubation. The untreated plants are dead because of the late blight disease. The treated plants are rated for percent of foliage which is healthy (percent disease control). The curative action of the compounds of this invention is demonstrated in the following table.

10

<u>Compound</u>	<u>Percent Disease Control</u>
2-cyano-2-methoxyimino-N-methyl-carbamoylacetamide	99
2-cyano-N-ethylcarbamoyl-2-methoxyiminoacetamide	100
2-cyano-2-ethoxyimino-N-ethyl-carbamoylacetamide	100
20 2-cyano-2-methoxyimino-N-propyl-carbamoylacetamide	100
N-allylcarbamoyl-2-cyano-2-methoxyiminoacetamide	100
Water treatment check	0

EXAMPLE 11

A wettable powder formulation can be prepared as follows:

	<u>Percent</u>
2-cyano-2-methoxyimino-N-propylcarbamoylacetamide	80
30 sodium alkyl naphthalenesulfonate	2
sodium ligninsulfonate	2
synthetic amorphous silica	3
Kaolinite	13

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The ingredients are thoroughly blended, passed through a hammer-mill to produce an average particle size under 40 microns, reblended and sifted through a U.S.S. No. 50 sieve (0.3 mm openings) before packaging.

This formulation can be applied as follows: A potato field is selected in which there is a uniform but light infection of the late blight disease. The older foliage of each plant supports one or two sporulating Phytophthora infestans lesions. The plant damage at this point is slight, but the potential for disease spread is high. Plots are designated as five rows wide and 20 meters long. Treatments are assigned to various plots randomly through the field leaving much of the field untreated as buffers between treated plots. A series of treatments is selected for application immediately following weather conditions conducive to disease spread. Among those treatments is the formulation of this Example dispersed in water at a concentration of 300 ppm of active ingredient. Other treatments are a representation of commercially available fungicides such as maneb, captfol, and chlorothalonil, applied at their recommended use rate. In addition to those single compound applications, combinations of the formulation of this Example with each of the commercial fungicides are made at rates of 1/2 of that used alone. Spray applications are made immediately after an overnight rain which had the potential of spreading the disease. After a week, the untreated foliage in this field is completely killed by the late blight disease. Those plots receiving treatments of commercial fungicides are severely diseased and are more than 80% defoliated. Those plots receiving the formulation of this Example are protected from the late blight disease and are only slightly defoliated. Those plots

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receiving the combination of the formulation of this invention plus a commercial fungicide are healthy and free of disease. The other compounds of this invention may be substituted with like results.

EXAMPLE 12

A wettable powder can be prepared as follows:

	<u>Percent</u>
2-cyano-N-ethylcarbamoyl-2-methoxyiminoacetamide	80
10 sodium dioctyl sulfosuccinate	1
sodium ligninsulfonate	2
attapulgate	17

The ingredients are blended and passed through a hammer mill fitted with a coarse screen. After reblending, it is finely ground in a hammer mill and packaged.

Greenhouse grown grape plants are inoculated by spraying with a spore suspension of Plasmopara viticola, downy mildew. After 10 hours incubation in a 20°C. saturated humidity chamber, six of the plants are sprayed to run-off with the above formulation dispersed in water to give 100 ppm active ingredient. Treatments with maneb at 2000 ppm active are made on similar plants. After two weeks incubation in a greenhouse, the untreated plants and plants treated with maneb are severely infected with downy mildew (90 percent of the susceptible leaves are defoliated). Plants treated with the above formulation are free of disease, demonstrating the curative effect.

EXAMPLE 13

A wettable powder can be prepared as follows:

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	Percent
2-cyano-N-ethylcarbamoyl-2-methoxy- iminoacetamide	12
manganese ethylene bisdithiocarbamate (maneb)	78
paraformaldehyde	1
sodium ligninsulfonate	1
zinc sulfate	1
sodium alkylnaphthalene sulfonate	0.5
10 methyl cellulose	0.25
kaolinite	6.25

The ingredients are blended and finely ground in a hammer mill to produce a wettable powder practically all of which will pass through a U.S.S. #100 screen (0.149 mm openings).

The above formulation is dispersed in a spray tank to give a concentration of 200 ppm active 2-cyano-N-ethylcarbamoyl-2-methoxyiminoacetamide. The maneb is also an active component in this formulation. This mixture is compared with treatments of an equal amount of maneb (1300 ppm) and maneb at double that concentration (2600).

Tomato plants growing uniformly in a field are inoculated with a spore suspension of P. infestans during a light rain which keeps the foliage wet overnight. The field is divided into plots so that each treatment can be replicated on four different plots. Treatments are applied as a spray to run off the day after the inoculation. Additional applications are made at 7 to 10 day intervals and in each case the sprays follow a natural or artificial (sprinkler) inoculation period by one or two days. By the end of the test period the untreated plants are more than 90% defoliated by late blight infections. The plants which

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are treated with maneb at 1300 ppm are more than 50% defoliated and those treated with maneb at 2600 ppm are about 30% defoliated. In contrast, the mixture in this formulation containing the active ingredient of this invention is so effective in curing established infections and preventing new infections that only an occasional lesion can be found in plots treated with this mixture.

10 The manganese ethylenebisdithiocarbamate in the above formulation can be replaced with similar amounts of commercial solid formulations of 2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil); N-(trichloromethylthio)-phthalimide (folpet); cis-N-[(1,1,2,2-tetrachloroethyl)-thio]-4-cyclohexene-1,2-dicarboximide (captafol); zinc ethylene bisdithiocarbamate; fixed copper, such as basic copper sulfate, basic copper carbonate, copper oxychloride, and/or copper oxide; triphenyltin hydroxide; or the co-ordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb).

EXAMPLE 14

20 In this Example, grape vines spray treated with a combination of this invention were healthier than comparable vines treated with either of the components of the combination. Individual vines in a vineyard near Bordeaux, France, were treated with test materials alone or in combinations at concentrations listed in the table below. Treatments were applied on a weekly schedule starting July 7. Each treatment was applied to 10 replicate vines. Natural infection by the grape downy mildew fungus, Plasmopora viticola, resulted in disease on over 50 percent of the leaves of untreated vines on August 27 when all vines were rated for

30

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infection. Both of the components of the combination reduced the disease incidence and the combinations almost eliminated all infection.

TABLE

<u>Material</u>	<u>gm. active ingredient/ 100 liters</u>	<u>Percent of leaves in- fected by P. viticola</u>
I)	20	20
10	40	15
	60	12
B)		
mancozeb	80	21
	120	20
	160	20
I + B)	10 160	1.8
	15 120	1.8
	20 80	2.5
Untreated	-- --	58

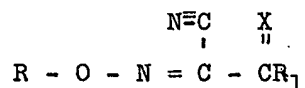
- 20 I) 2-Cyano-N-(ethylcarbamoyl)-2-methoxyiminoacetamide.
 B) Co-ordination product of zinc ion and manganese ethylene
 bisdithiocarbamate (mancozeb).

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A composition useful for controlling fungus disease in plants consisting essentially of an inert diluent and a compound of the formula



wherein R is hydrogen; alkyl of 1 to 13 carbon atoms; alkyl of 1 to 13 carbon atoms substituted with alkoxy, acyl of 2 to 4 carbon atoms, acyloxy of 2 to 4 carbon atoms or cyano; acyl of 1 to 4 carbon atoms; alkoxy, acyl of 2 to 4 carbon atoms; aralkyl of 7 to 10 carbon atoms; or a metal selected from the group consisting of sodium, potassium, calcium, manganese, zinc, copper and iron;

R₁ is alkoxy of 1 to 4 carbon atoms or -NR₂R₃;

R₂ is hydrogen, alkyl of 1 to 4 carbon atoms, alkoxy-carbonyl of 2 to 4 carbon atoms or $-\text{CN} \begin{array}{l} \text{O} \\ \text{||} \\ \text{R}_4 \\ \text{R}_5 \end{array}$;

R₃ is hydrogen or alkyl of 1 to 4 carbon atoms with the proviso that R₃ is H when R₂ is alkoxy-carbonyl or $-\text{CN} \begin{array}{l} \text{O} \\ \text{||} \\ \text{R}_4 \\ \text{R}_5 \end{array}$;

R₄ is hydrogen or alkyl of 1 to 4 carbon atoms;

R₅ is hydrogen or alkyl of 1 to 4 carbon atoms; and

X is oxygen or sulfur.

2. The composition of Claim 1 wherein X is oxygen; R is hydrogen, alkyl of 1 to 13 carbon atoms, acyl of 1 to 4 carbon atoms, alkoxy-carbonyl of 2 to 4 carbon atoms, or a metal selected from the group consisting of sodium, potassium, calcium, manganese, zinc, copper, and iron; and R₁ is -NH₂,

O
||
NHCH₃ or -NHC-NH₂.

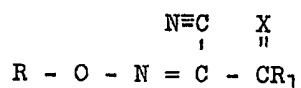
3. The composition of Claim 2 wherein R is hydrogen, alkyl of 1 to 13 carbon atoms, or acetyl.

4. A method of controlling fungus disease in plants consisting essentially of applying to the locus to be protected an effective amount of the composition of Claim 1.

5. A method of controlling fungus disease in plants consisting essentially of applying to the locus to be protected an effective amount of the composition of Claim 2.

6. A method of controlling fungus sideases in plants consisting essentially of applying to the locus to be protected an effective amount of the composition of Claim 3.

7. In a fungicidal composition the improvement consisting essentially of incorporation of a compound of the formula

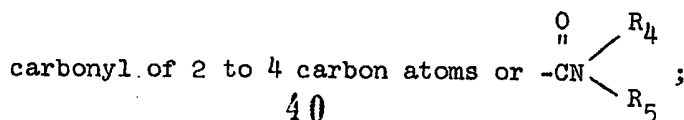


wherein R is hydrogen; alkyl of 1 to 13 carbon atoms;

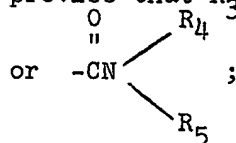
alkyl of 1 to 13 carbon atoms substituted with alkoxy carbonyl of 2 to 4 carbon atoms, acyl of 2 to 4 carbon atoms, acyloxy of 2 to 4 carbon atoms or cyano; acyl of 1 to 4 carbon atoms; alkoxy carbonyl of 2 to 4 carbon atoms; aralkyl of 7 to 10 carbon atoms; or a metal selected from the group consisting of sodium, potassium, calcium, manganese, zinc, copper and iron;

R₁ is alkoxy of 1 to 4 carbon atoms or -NR₂R₃;

R₂ is hydrogen, alkyl of 1 to 4 carbon atoms; alkoxy-



R_3 is hydrogen or alkyl of 1 to 4 carbon atoms, with the proviso that R_3 is hydrogen when R_2 is alkoxy carbonyl



R_4 is hydrogen or alkyl of 1 to 4 carbon atoms;

R_5 is hydrogen or alkyl of 1 to 4 carbon atoms;

X is oxygen or sulfur.

8. The composition of Claim 2 wherein R is hydrogen and R_1 is NH_2 , 2-cyano-2-hydroxyiminoacetamide.

9. The composition of Claim 2 wherein R is sodium and R_1 is NH_2 , 2-cyano-2-hydroxyiminoacetamide, sodium salt.

10. The composition of Claim 2 wherein R is methyl and R_1 is NH_2 , 2-cyano-2-methoxyiminoacetamide.

11. The composition of Claim 2 wherein R is methyl and R_1 is $\begin{array}{c} \text{O} \\ || \\ \text{H} \end{array} - \text{N} - \text{CNH}_2$, N-carbamoyl-2-cyano-2-methoxyiminoacetamide.

12. The composition of Claim 2 wherein R is acetyl, and R_1 is $-\text{NHCH}_3$, 2-acetoxyimino-2-cyano-N-methylacetamide.

13. A method of controlling fungus disease in plants consisting essentially of applying to the locus to be protected an effective amount of the composition of Claim 8.

14. A method of controlling fungus disease in plants consisting essentially of applying to the locus to be protected an effective amount of the composition of Claim 9.

15. A method of controlling fungus disease in plants consisting essentially of applying to the locus to be protected an effective amount of the composition of Claim 10.

16. A method of controlling fungus disease in plants consisting essentially of applying to the locus to be protected an effective amount of the composition of Claim 11.

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17. A method of controlling fungus disease in plants consisting essentially of applying to the locus to be protected an effective amount of the composition of Claim 12.

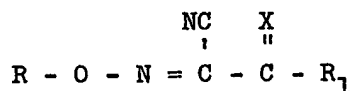
18. The composition of Claim 1 containing an adjuvant selected from the group consisting of surfactants, water soluble film-forming polymers, humectants and non-phytotoxic oils.

19. A fungicidal composition comprising the composition of Claim 1 in combination with a fungicide selected from the group consisting of bis(dimethylthiocarbamoyl)disulfide; or tetramethylthiuram disulfide (thiram); metal salts of ethylene-bisdithiocarbamic acid or propylenebisdithiocarbamic acids, e.g. manganese, zinc, iron and sodium salts (maneb or zineb); n-dodecylguanidine acetate (dodine); N-(trichloromethylthio)phthalimide (folpet); N-[(trichloromethyl)thio]-4-cyclohexene-1,2-dicarboximide (captan); cis-N-[(1,1,2,2-tetrachloroethyl)thio]-4-cyclohexene-1,2-dicarboximide (captofol); 2,4-dichloro-6-(o-chloroanilino)- α -triazine; 3,3'-ethylenebis(tetrahydro-4,6-dimethyl-2H-1,3,5-thiadiazine-2-thione), (milneb); triphenyltin hydroxide (fentin hydroxide); triphenyltin acetate (fentin acetate); N'-dichlorofluoromethylthio-N,N-dimethyl-N'-phenylsulfamide (dichlofluanid); tetrachloroisophthalonitrile (chlorothalonil); tribasic copper sulfate; fixed copper; sulfur; methyl-1-(butylcarbamoyl)-2-benzimidazolecarbamate (benomyl); methyl-2-benzimidazolecarbamate; and 1,2-bis(3-methoxycarbonyl-2-thioureido)benzene (methyl thiophanate).

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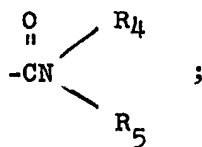
CLAIMS SUPPORTED BY THE SUPPLEMENTARY DISCLOSURE

20. A composition useful for controlling fungus disease in plants consisting essentially of an inert diluent and a compound of the formula

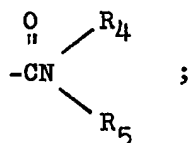


wherein R is hydrogen; alkyl of 1 to 13 carbon atoms; alkyl of 1 to 13 carbon atoms substituted with alkoxy carbonyl of 2 to 4 carbon atoms, acyl of 2 to 4 carbon atoms, acyloxy of 2 to 4 carbon atoms, or cyano; acyl of 1 to 4 carbon atoms; alkoxy carbonyl of 2 to 4 carbon atoms; cycloalkyl of 5 to 7 carbon atoms; alkenyl of 3 to 6 carbon atoms; aralkyl of 7 to 10 carbon atoms; or a metal selected from the group consisting of sodium, potassium, calcium, manganese, zinc, copper and iron;

R_1 is alkoxy of 1 to 4 carbon atoms or NR_2R_3 ;
 R_2 is hydrogen, alkyl of 2 to 4 carbon atoms, alkoxy carbonyl of 2 to 4 carbon atoms or



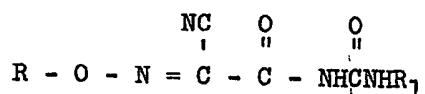
R_3 is hydrogen or alkyl of 1 to 4 carbon atoms with the proviso that R_3 is H when R_2 is alkoxy carbonyl or



R_4 is hydrogen, alkyl of 1 to 4 carbon atoms or allyl;
 R_5 is hydrogen or alkyl of 1 to 4 carbon atoms; and
X is oxygen or sulfur.

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21. A composition useful for controlling fungus disease in plants consisting essentially of an inert diluent and a compound of the formula



wherein R is hydrogen, alkyl of 1 to 13 carbon atoms, cycloalkyl of 5 to 7 carbon atoms or alkenyl of 3 to 6 carbon atoms; and

R₁ is hydrogen, alkyl of 1 to 4 carbon atoms or allyl provided that when R is alkyl, R₁ is allyl.

22. A composition of Claim 21 wherein the compound is 2-cyano-2-methoxyimino-N-methylcarbamoylacetamide.

23. A composition of Claim 21 wherein the compound is 2-cyano-N-ethylcarbamoyl-2-methoxyiminoacetamide.

24. A composition of Claim 21 wherein the compound is 2-cyano-2-ethoxyimino-N-ethylcarbamoylacetamide.

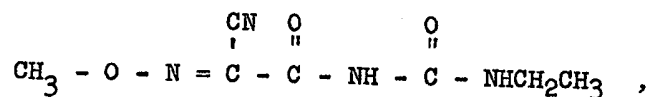
25. A composition of Claim 21 wherein the compound is 2-cyano-2-methoxyimino-N-propylcarbamoylacetamide.

26. A composition of Claim 21 wherein the compound is N-allylcarbamoyl-2-cyano-2-methoxyiminoacetamide.

27. A method of controlling fungus disease in plants consisting essentially of applying to the locus to be protected a fungicidal composition of Claim 20.

28. A method of controlling fungus disease in plants consisting essentially of applying to the locus to be protected a fungicidal composition of Claim 21.

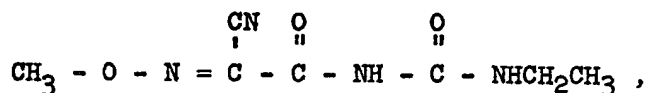
29. A fungicidal combination consisting essentially of



a diluent and a fungicide selected from manganese ethylenebis-dithiocarbamate, admixed with inorganic zinc salts; co-

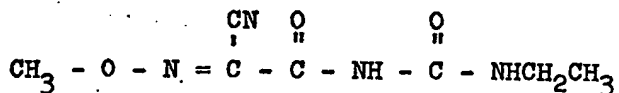
ordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb); zinc ethylene bisdithiocarbamate; fixed copper, such as basic copper sulfate, basic copper carbonate, copper oxychloride, and/or copper oxide; N-(trichloromethylthio)-phthalimide (folpet); 2, 4,5,6-tetrachloroisophthalonitrile (chlorothalonil); and cis-N-[(1,1,2,2-tetrachloroethyl)thio]-4-cyclohexene-1,2-dicarboximide (captafol).

30. A fungicidal combination consisting essentially of



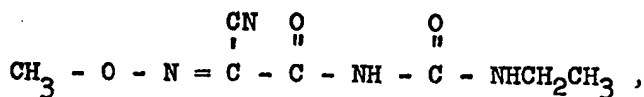
a diluent and a fungicide selected from manganese ethylenebis-dithiocarbamate, admixed with inorganic zinc salts; co-ordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb); fixed copper, such as basic copper sulfate, basic copper carbonate, copper oxychloride, and/or copper oxide; N-(trichloromethylthio)phthalimide (folpet); and triphenyltin hydroxide.

31. A fungicidal combination consisting essentially of



and co-ordination product of zinc ion and manganese ethylene-bisdithiocarbamate (mancozeb).

32. A fungicidal composition consisting essentially of



co-ordination product of zinc ion and manganese ethylenebis-dithiocarbamate (mancozeb), and fixed copper.

33. A method for the inhibition of fungus diseases in plants comprising applying to the locus of such disease a fungicidally effective amount of a combination of Claim 29.

34. A method for the inhibition of fungus diseases in plants comprising applying to the locus of such disease a fungicidally effective amount of a combination of Claim 30.

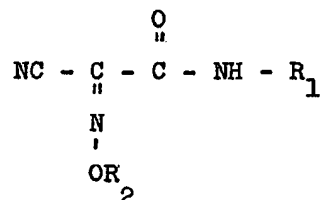
35. A method for the inhibition of fungus diseases in plants comprising applying to the locus of such disease a fungicidally effective amount of a combination of Claim 31.

36. A method for the inhibition of fungus diseases in plants comprising applying to the locus of such disease a fungicidally effective amount of a combination of Claim 32.

37. A fungicidal composition comprising the composition of Claim 29 in combination with a fungicide selected from the group consisting of bis(dimethylthiocarbamoyl)disulfide; or tetramethylthiuram disulfide (thiram); metal salts of ethylenebisdithiocarbamic acid or propylenebisdithiocarbamic acids, e.g. manganese, zinc, iron and sodium salts (maneb or zineb) alone or admixed with zinc salts; co-ordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb); n-dodecylguanidine acetate (dodine); N-(trichloromethylthio)phthalimide (folpet); N- γ -(trichloromethyl)thio- γ -4-cyclohexene-1,2-dicarboximide (captan); cis-N- γ -(1,1,2,2-tetrachloroethyl)thio- γ -4-cyclohexene-1,2-dicarboximide (captofol); 2,4-dichloro-6-(o-chloroanilino)- α -triazine; 3,3'-ethylenebis(tetrahydro-4,6-dimethyl-2H-1,3,5-thiadiazine-2-thione), (milneb); triphenyltin hydroxide (fentin hydroxide); triphenyltin acetate (fentin acetate); N'-dichlorofluoromethylthio-N,N-dimethyl-N'-phenylsulfamide (dichlorfluanid); tetrachloroisophthalonitrile (chlorothalonil); tribasic copper sulfate; fixed copper; sulfur; methyl-1-(butylcarbamoyl)-2-benzimidazolecarbamate (benomyl); methyl-2-benzimidazolecarbamate; and 1,2-bis(3-methoxycarbonyl-2-thioureido)benzene (methyl thiophanate).

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38. A fungicidal composition containing as active substance a compound of the formula



wherein $\text{R}_1 = \text{H}$ or aminocarbonyl

$\text{R}_2 = \text{H}$ or a metal ion

together with an inert diluent or an inert diluent and a surface activating agent.

39. A method of controlling fungus disease in plants which comprises applying to plants a composition of claim 38.



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